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s^Pi Plastics Engineering Handbook

**of the Society of the
Plastics Industry, Inc.**

Fifth Edition

Edited by

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condition, they can be formed to the finished product shape with or without pressure and polymerized by using chemicals or heat.

The distinction between thermoplastics and thermosets is not always clearly drawn. For example, thermoplastic polyethylene can be extruded as a coating for wire and subsequently crosslinked (either chemically or by irradiation) to form a thermoset material that no longer will melt when heated. Some plastic materials even have members in both families; there are, for instance, both thermoset and thermoplastic polyester resins.

THERMOPLASTIC RESINS

The first thermoplastics discussed in this section are the so-called commodity thermoplastics and their chemical relatives. These polymers have found their way into wide commercial use, with millions of tons produced annually. Their ranks include the polyolefins, the styrenics, and the vinyls. Also covered here are the acrylics and the cellulosics.

The remaining thermoplastic materials generally are categorized as engineering resins or engineering thermoplastics (ETPs). These resins are produced in substantially smaller quantities than the commodity thermoplastics, are priced higher, and tend to compete with metals rather than with glass, paper, and wood, as the commodities do.

Discussions of thermoplastic elastomers and of alloys and blends concludes the section, along with a list of some types of these materials that have been commercialized to date.

The Polyolefins

Polyethylenes. Polyethylenes are characterized by toughness, near-zero moisture absorption, excellent chemical resistance, excellent electrical insulating properties, low coefficient of friction, and ease of processing.

In general, they are not outstanding load-bearing materials, but high-density polyethylene can be used for some short-term light loads.

Few thermoplastics have the excellent chemical resistance and dielectric properties of polyethylenes. Soluble in some organic solvents

above 140°F, polyethylenes resist bases and acids at room temperature. Their resistivity (both volume and surface) and dielectric strength are high.

Polyethylenes can be crosslinked to form infusible thermosetting materials with high heat resistance and crack resistance. Applications are in wire and cable coating, foams, and rotationally molded products.

Polyethylenes are classified by density as follows: (a) 0.880 to 0.915 g/cu cm (called ultra- or very low density), (b) 0.910 to 0.925 g/cu cm (low density), (c) 0.926 to 0.940 g/cu cm (medium density), and (d) 0.941 to 0.965 g/cu cm (high density). The primary differences among the types are in rigidity, heat resistance, chemical resistance, and ability to sustain loads. In general, as density increases, hardness, heat resistance, stiffness, and resistance to permeability increase. So-called conventional low-density polyethylenes (LDPE) are produced in high-pressure reactors. Such polymers have highly branched structures with moderate crystallinity (50-65%).

Low-density polyethylenes are quite flexible, with high impact strength and relatively low heat resistance (maximum recommended service temperature is 140-175°F), although grades are available with heat resistance up to 200°F.

Traditional markets for LDPE are in packaging films, extrusion coating of paper, wire and cable coating, injection molding, and pipe and tubing. Since the introduction of linear low-density polyethylene (see below), conventional LDPE has been gradually displaced in some of these areas.

The high-pressure route also is used to make copolymers of ethylene with polar monomers such as vinyl acetate or ethyl acrylate. The EVAs and EEAs that are produced have low-temperature flexibility and are used in tough films and as a component of multilayer constructions for low-temperature heat sealing. Acid copolymers (with acrylic or methacrylic acid) are used for their hot tack and adhesive properties. Neutralized with metallic ions, these materials become clear ionomers, used in coating applications.

Linear polyethylenes, as the name suggests,

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have very little branching along the polymer chains. The polymerization of linear polyethylenes at low pressures has been used to manufacture high-density resins since the mid-1950s. Methods for making linear low-density polyethylenes (LLDPE) did not become commercial until the 1970s.

Commercial LLDPE resins are made in gas-phase reactors; the polymers typically contain up to 10% alpha olefin comonomers (butene, hexene, methyl pentene, or octene). The reactor output is in granular form, but normally is extruded and pelletized to incorporate additive systems.

LLDPE polymers, with little long-chain branching, have much greater elongation than LDPE. Their higher tear, tensile, and impact strength, along with improved resistance to environmental stress cracking, allow stronger products to be produced with less material. This has been particularly important in film markets, where considerable downgauging has been accomplished. (See Fig. 3-1.) Ultra- and very

low-density polyethylenes (ULDPE and VLDPE) are essentially synonymous designations for linear polyethylenes with densities down to 0.880 g/cu in. Produced in gas-phase reactors, they are finding application as impact modifiers for other polyolefins and in film and sheet markets.

Linear high-density polyethylene (HDPE) can be produced via a slurry process or in gas-phase reactors identical to those used to make LLDPE. HDPE polymers are highly crystalline, tough materials that can be formed by most processing methods. Much HDPE is blow-molded into containers for household and industrial chemicals. It is injection-molded into items such as crates, housewares, pails, and dunnage containers; extruded into pipe, tubing, and wire insulation; blown into film for packaging; and rotationally molded into containers, toys, and sporting goods. (See Fig. 3-2.)

Within the density range of HDPEs, the stiffness, tensile strength, melting point, and chemical resistance all improve at the high end. However, materials with the highest densities have lower stress crack resistance and low-temperature impact strength.

High molecular weight HDPE polymers are a special class of linear resins with molecular weights in the 200,000 to 500,000 range. To obtain processability along with end-use properties, control of the molecular weight distribution is critical. Some materials are produced with a "bimodal" molecular weight distribution to obtain the necessary balance.

HMW-HDPE is made into blown film for packaging, extruded into pressure pipe, and blow-molded into large shipping containers. Extruded sheet is used to form truck bed liners and pond liners.

At the highest end of the spectrum is ultra-high molecular weight high-density polyethylene. Its weight average molecular weight is over 3 million. Because the resin does not flow when melted, it normally is compression-molded into thick sheets or ram-extruded.

High strength, chemical resistance, and lubricity make UHMW-HDPE ideal for gears, slides, rollers, and other industrial parts. It also is used to make artificial hip joints. In fiber form, the UHMW-HDPE's linear structure exhibits liquid crystal properties that are useful in



Fig. 3-1. Bag for ice cubes from linear low density polyethylene. (Courtesy of Union Carbide Chemicals and Plastics)

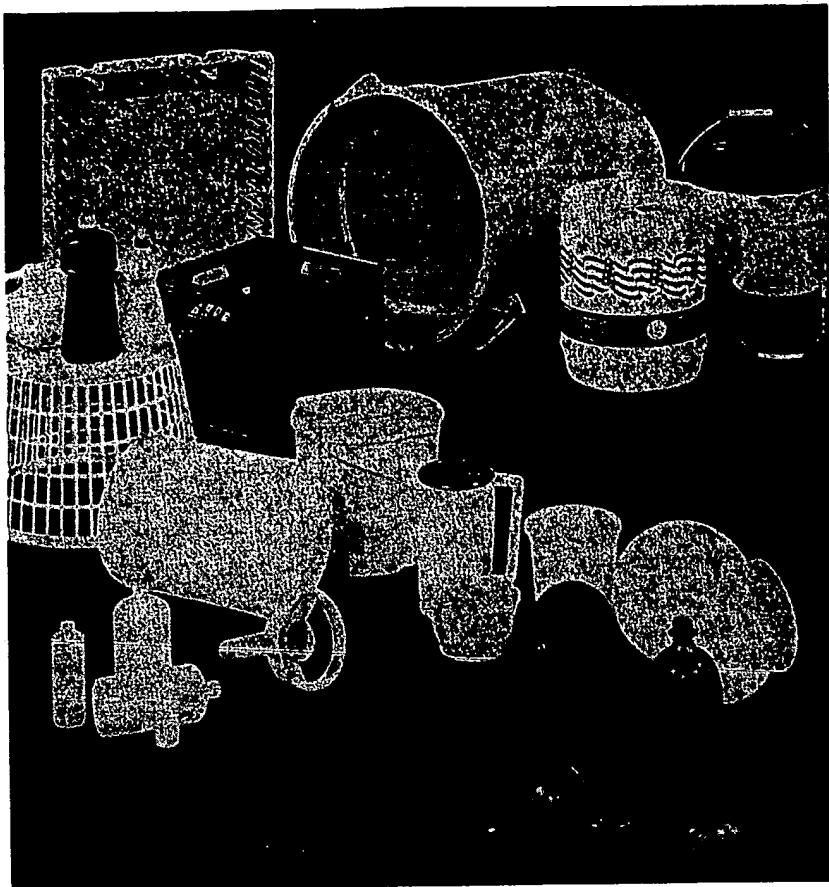


Fig. 3-2. Examples of high-density polyethylene products. (Courtesy of Union Carbide Chemicals and Plastics)

reinforcing composite structures. The fiber also can be woven into lightweight ultrastrong fabrics.

Polymethylpentene (PMP). Based on 4-methylpentene-1, this crystalline polyolefin is characterized by transparency (90% light transmission), low specific gravity (0.83), and a high melting point (464°F). Its drawbacks are brittleness and poor UV resistance. PMP has found application in making injection-molded and blow-molded laboratory ware and medical products, food processing equipment, and microwavable packaging. Glass fiber-reinforced grades, with heat distortion temperatures up to 440°F, can compete with more expensive engineering resins for electrical/electronic and automotive applications.

Polypropylene. This polyolefin has turned out to be the most versatile of the family, accounting for the continuing rapid increase in its use. First produced in the 1950s, early polypropylenes (PPs) suffered from low yields in polymerization, high percentage (about 10%) of atactic polymer, and poor control of molecular weight.

The development of high-activity catalysts in the 1970s improved the yields dramatically and almost eliminated production of the atactic form. The resulting isotactic polymers were highly stereoregular.

Polypropylenes have better resistance to heat (heat distortion temperature at 66 psi: 200–250°F) and resist more chemicals than do other thermoplastic materials of the same cost. Also, polypropylenes have negligible water absorption and excellent electrical properties, and they are easy to process.